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(Sch 55971 IV/53f)

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Verfahren zur Herstellung einer festen, schokoladeartigen Guß- oder Glasurmasse
für Konditoreiwaren.

Patentiert im Deutschen Reiche vom 21. August 1919 ab.

Die Erfindung betrifft ein Verfahren zur Herstellung einer festen, schokoladeartigen Guß- oder Glasurmasse für Konditoreiwaren. Das mittels dieses Verfahrens hergestellte Produkt bildet im Gegensatz zu ähnlichen Produkten eine feste, nicht klebrig werdende Masse, die bei der Verwendung leicht angewärmt und dadurch flüssig wird und auf den Konditorwaren einen glänzenden Überzug bildet.

Das Verfahren besteht darin, daß eine allmählich hergestellte Mischung von bestimmten Mengen dünnflüssigem Blockkakao und Zucker mit heißem Wasser unter Zusatz von Vanille schnell auf 88 bis 90° erhitzt wird, worauf nach dem Verkochen die Masse rasch auf 35° abgekühlt und mittels eines langen Holzspachtels in bekannter Weise tabliert wird.

Ein Ausführungsbeispiel des Verfahrens ist folgendes:

Etwa 2 kg Blockkakao werden unter geringer Hitze zerlaufen gelassen, bis die Masse dünnflüssig geworden ist, worauf von etwa 5 kg Zucker zuerst ein Drittel darunter gemischt und genügend verrührt und nun der dritte Teil von $3\frac{3}{4}$ l heißem Wasser hinzugegossen wird. Das Zugießen muß nach und nach geschehen, da beim plötzlichen Hinzugießen der ganzen Menge keine Bindung entsteht und die Masse vor dem Kochen schon zusammenfahren würde und dann nicht wieder glatt zu bringen ist.

Zu dieser Mischung wird von der Wasser- und Zuckermenge ein weiteres Drittel Zucker

und ein Drittel Wasser hinzugesetzt und so abwechselnd auch das letzte Drittel, bis Zucker und Wasser aufgebraucht sind. Zu der Masse werden jetzt zwei der Länge nach durchgeschnittene Schoten Vanille gelegt, damit sie derselben beim Kochen den erforderlichen guten Geschmack verleihen.

Die ganze Masse wird nun einer größeren Hitze ausgesetzt, um sie schnell auf 88 bis 90° des Zuckerthermometers zu erhitzen. Während dieses Erhitzens darf die Masse nicht mehr gerührt werden, jedoch müssen Vorkehrungen getroffen werden, die ein Anbrennen der Masse verhüten, was z. B. durch Zwischenlegen eines Schamottesteins zwischen Hitzequelle und Kochkessel geschehen kann.

Sobald die Masse auf 88 bis 90° erhitzt ist, wird sie schnell auf 35° abgekühlt, was zweckmäßig durch Aufgießen auf eine mit Rand versehene Marmorplatte geschieht. Hierauf erfolgt in bekannter Weise das Tablieren mittels eines langen Holzspachtels durch Hin- und Herreiben, bis die Masse fest ist.

Diese feste Masse ist stets fertig zum Gebrauch, unbegrenzt lange haltbar und sparsam in ihrer Verwendung. Durch leichtes Anwärmen wird sie sofort wieder flüssig, es braucht dann nur so viel Läuterzucker hinzugerührt zu werden, wie für den auf der betreffenden Konditorware herzustellenden Überzug erwünscht ist. Übrigbleibende Rückstände werden getrocknet und können immer wieder verwendet werden, ohne daß vorher ein Kochen und Tablieren notwendig ist. Wenn

nicht die im vorliegenden Falle angegebenen Mengenverhältnisse verwendet werden und die Herstellung der Mischung und deren Abkühlung in der erwähnten bestimmten Weise
 5 erfolgen, so wird die gewünschte Wirkung nicht erreicht.

PATENT-ANSPRUCH:

10 Verfahren zur Herstellung einer festen, schokoladeartigen Guß- oder Glasurmasse für Konditoreiwaren, dadurch gekennzeichnet, daß einer durch Schmelzen von

etwa 2 kg Blockkakao erhaltenen Lösung der dritte Teil von etwa 5 kg Zucker und von etwa $3\frac{3}{4}$ l heißem Wasser nach und nach unter Umrühren zugesetzt und dieser
 15 Mischung hierauf abwechselnd die übrigen Teile Wasser und Zucker beigemischt werden, worauf nach Zusatz von Vanille unter Vermeidung des Anbrennens und
 20 ohne Umrühren die Masse schnell auf 88 bis 90° erhitzt, dann schnell auf etwa 35° abgekühlt und schließlich in bekannter Weise tabliert wird.

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(54) MODIFIED VEGETABLE FATS

(71) We, CADBURY INDIA LIMITED, a Company incorporated under the Indian Companies Act, of "Cadbury House", Bhulabhai Desair Road, Bombay 400 026, Maharashtra, India, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of modified vegetable fats capable of replacing at least part of the cocoa butter present in chocolate and other confectionary products.

Cocoa butter, the natural fat of cocoa bean (*Theobroma Cacao* L.) is an essential constituent of all chocolates and many other confectionary products. In the manufacture of high quality chocolates the roasted cocoa bean is shelled and the nib ground. To this ground nib, which is called cocoa liquor are added sugar, milk solids, cocoa butter, emulsifiers and flavourings. The physical characteristics of such chocolates arise mainly from the cocoa butter present. Cocoa butter melts completely at 35°C or slightly below body temperature; it is a hard brittle solid at normal room temperature. Cocoa butter is used in chocolates and confectionary products largely because its physical properties contribute to glossy coatings, absence of waxiness and favourable volume changes in the moulding operation.

A great deal of research work has been done by various workers to develop a substitute for at least part of the cocoa butter added during the manufacture of chocolate, i.e. a fat which can be used to make chocolate from partly or completely defatted ground cocoa bean or as a coating for confections. Oils and fats containing essentially C 16 and C 18 fatty acids would logically be preferred as raw materials for making cocoa butter substitutes. The most common of these are palm oil, cottonseed oil, Borneo tallow and mowrah fat.

The present invention provides a modified fat compatible with cocoa butter and having the following physical characteristics when admixed with cocoa butter and milk fat:—

1. A very short melting range,
2. Melting readily in the mouth with out have a waxy, taste,
3. Quick hardening,
4. Resistance to formation of grey cast and

surface bloom,

5. Compatibility with defatted cocoa powder, cocoa liquor and milk fat individually or in mixture, and 55

6. Controlled shrinkage during cooling for satisfactory mould release.

The essential characteristics and measurements necessary to determine the quality and suitability of a cocoa butter substitute for use in chocolate manufacture are:— 60

1. Melting behaviour,
2. Melting dilatation,
3. Hardness,
4. Solidification and super-cooling characteristics 65

5. Stability towards oxidative rancidity, and

6. Taste and appearance. 70

We have found that a cocoa butter substitute meeting the above mentioned requirements can be prepared from a vegetable fat, especially *Shorea Robusta* Seed Fat, containing substantial quantities of both disaturated and diunsaturated glycerides of C₁₆, C₁₈ and C₂₀ acids. 75

Sal, botanically known as *Shorea Robusta*, grows abundantly in the States of Madhya Pradesh, Uttar Pradesh, Orissa and Bihar in India. Cocoa butter is hard and brittle at 30°C. Unlike this, sal fat is greasy at this temperature. This fat crystallises in a coarse and grainy crystalline mass, occluding some liquid fat which tends to separate out on standing. For this reason, sal fat cannot be used as a complete substitute for cocoa butter, even though it melts within a narrow range of 26°C—38°C. 80

The present invention provides a process for the production of a modified vegetable fat which comprises partially hydrogenating a refined, bleached and deodorised vegetable fat containing glycerides of C₁₆, C₁₈ and C₂₀ fatty acids, in the presence of a metal hydrogenation catalyst, to obtain hardened fat and subjecting the said hardened fat to thermal crystallisation at a temperature of 30°C—40°C to remove higher melting glycerides until the remaining hardened fat has a melting point within the range from 30°C to 40°C. 90

The purpose of the partial hydrogenation is to harden the liquid fat that separates out from the crystallised sal fat thereby making the fat more stable towards oxidative rancidity and uniform in its consistency. The iodine value of 100

raw sal fat varies from 38 to 45. This variation in iodine number is due to the varying amounts of glycerides of polyunsaturated fatty acids present in the raw fat.

5 The hydrogenation is carried out using a conventional metal catalyst such as nickel, copper, palladium, platinum or a complex catalyst such as copper chromium using a support of Kieselguhr or any other diatomaceous earth.

10 The amount of catalyst used is not critical and may be varied, say from 0.05% to 2% by weight or even more, but the usual range is 0.05 to 1%. The hydrogenation reaction is preferably carried out using a supported fresh nickel catalyst and the suitable temperature range is from 15 about 100°C–180°C. The reaction is carried out at pressures preferably not exceeding 50 lb per sq. in., and more preferably between atmospheric and 35 lb per sq. in. The time of hydrogenation may vary, e.g., from about 10 minutes 20 to about an hour or more according to the iodine value of the raw material. The hydrogenated fat should preferably contain less than 2% of trisaturated glycerides.

25 The thermal crystallisation is so devised that 10 to 20% of the high melting glycerides by weight of the hardened sal fat is removed. The removal of high melting glycerides from hardened sal fat is essential to obtain a low 30 melting fraction which melts sharply at body temperature and is free from any waxiness. In order to achieve this the hardened sal fat is kept under controlled temperature in the melted form, when the high melting glycerides crystallise and settle at the bottom of the crystallisation vessel. This high melting fraction can find 35 an application as a seeding material in the thermal crystallisation technique. A suitable temperature range for thermal crystallisation is, for example, from about 30°C–40°C, particularly 40 33°C–38°C; and especially 34°C–36°C. The time required for the thermal crystallisation of high melting glycerides may vary, e.g. from about 36 hours to 72 hours or more depending 45 on the temperature range chosen and/or the desired percentage of the high melting glycerides to be removed. The iodine value of the desired low melting fraction may vary from about 37 to 40.

50 Undesirable tannins and phenols, especially ellagic acid, generally occur in raw vegetable fats, for example raw sal fat. Ellagitannins are complex ester glycosides and occur largely in myrobalans and oak galls. The deposition of 55 ellagic acid is one of the causes of the unappetizing haziness which sometimes develops in fruit juices.

According to the present invention, in order to remove ellagic acid and ellagitannins from 60 raw sal fat, a reagent containing sodium acetate and acetic acid buffer (pH 4.5) is used. This reagent is added to the raw sal fat to an extent of 0.5% to 2% by weight as a 10% solution, as described and claimed in our copending application No. 4126/78, Serial No: 1564681. This 65

reagent complexes the ellagic acid present in the raw sal fat and removes it. The removal of ellagic acid from raw sal fat by this procedure has been confirmed by using spectrophotometric techniques.

Other vegetable fats such as mowrah, phulwara and mango kernel fat can also be used as starting materials individually or in combination with one another or with sal fat for preparation of a cocoa butter-like fat by adopting similar steps such as hydrogenation 75 followed by fractionation by thermal crystallisation.

The following Example, in which all parts are by weight, illustrates the invention.

EXAMPLE

A sample of raw sal fat was treated with sodium acetate-acetic acid reagent and then washed with warm water.

On analysis by spectrophotometry it was 85 noticed that after the pretreatment of the raw sal fat with the sodium acetate-acetic acid reagent the absorbance at 255 mμ and 366 mμ due to phenols similar to ellagic acid and ellagic acid and ellagitannins, was found to have undergone a sharp reduction.

Neutralisation of the degummed sal fat was carried out with 10% aqueous caustic soda solution at 40°C. The acid value of the neutralised fat was 0.15. Bleaching of the neutralised fat was carried out at 80°C using activated earth (2% to 5%) and activated carbon (0.2 to 1%) 95 under high vacuum.

The refined and bleached sal fat was then hydrogenated at 135°C in the presence of 100 0.5% of a fresh nickel catalyst containing 18% Ni on Kieselguhr, at a gauge pressure of 20 lb per sq. in., for a period of 40 minutes in a pressure vessel with stirring, until the iodine value of the fat reached the desired range 33 to 36. Under these conditions of hydrogenation the trans-isomer content of the product, measured by infra-red absorption spectrophotometry, was about 2% of the total hydrogenated material. The hydrogenated 105 fat was filtered to remove the nickel catalyst and then post-bleached to remove traces of nickel using bleaching earth. The hardened fat was fractionated by thermal crystallisation for 48 hours at 37°C to remove high melting glycerides. The high melting glycerides (15%) that crystallised were removed by filtration and the low melting fraction (85%) consisted of the desired fraction having previously 110 stated characteristics.

The modified vegetable fat thus prepared is harder than cocoa butter at all temperatures up to its melting temperature in the neighbourhood of 37°C. This fat melts sharply at 37°C. This is higher than that of cocoa butter by 2°C, 125 a desirable characteristic for tropical countries. This fat exhibited a polymorphic behaviour similar to that of cocoa butter, with no liquid phase separating at ambient temperatures. It is also compatible with cocoa butter in all pro- 130

portions without formation of eutectics. The substitute fat exhibited a temperature rise of 4.0°C–5.0°C on solidification as compared with approximately 5°C for cocoa butter.

5 The substitute was then tested for cooling curve (Figure 1 of the accompanying drawings), dilatation (Figure 2) and thermal profile by differential scanning calorimetry for cocoa butter (Figure 3) and sal fat (Figure 4).

10 The dilatation tests were carried out by cooling the melted fat to 0°C for 90 minutes, tempering it for 48 hours at 26°C and again cooling to 0°C before measuring the dilatation at various temperatures. The dilatation results for the substitute along with that of cocoa butter are given below in Table 1. Dilatation is the isothermal melting expansion expressed in cubic millimetres and referred to 25 g of material.

TABLE 1

<i>Dt.</i>	<i>Modified Fat</i>	<i>Cocoa Butter</i>
D ₂₀	2190	2025
D ₂₅	1588	1558
D ₃₀	1132	1118
25 D ₃₅	50	10
D ₄₀	2	0
D ₄₅	0	0

The Jensen cooling curve of the cocoa butter replacement was determined as follows:—

30 About 75 g of sample was heated well above its melting point and placed in a test tube (length — 10 cm), a glass loop stirrer and a thermometer were inserted and the assembly was immersed in an air bath at 17°C. The sample was stirred at the rate of six strokes per minute until solidification occurred. A similar trial was carried out with a sample of cocoa butter and the cooling curves of temperature against time for each sample was plotted. These curves are shown in Figure 1 of the accompanying drawings in which curve 1 indicates the temperature rise on solidification in the case of cocoa butter and curve 2 indicates the same for the modified fat.

45 The above mentioned modified vegetable fat comprising low melting fraction was used at various levels such as 5, 10, 15, 20 and 25% by replacing cocoa butter in the manufacture of chocolates. Chocolates so manufactured were found to have similar physical and moulding characteristics to those of standard chocolates. WHAT WE CLAIM IS:

1. A process for the production of a modified vegetable fat which comprises partially hydrogenating a refined, bleached and deodorised vegetable fat containing glycerides of C₁₆, C₁₈ and C₂₀ fatty acids, in the presence of a metal hydrogenation catalyst to obtain hardened fat and subjecting the said hardened fat to thermal crystallisation at a temperature of 30°C–40°C to remove higher melting glycerides until the remaining hardened fat has a melting point within the range from 30°C to 40°C.

65 2. A process according to claim 1, wherein

the vegetable fat is a fat of sal seed, mowrah, phulwara or mango kernel.

3. A process according to claim 1 or 2, wherein the vegetable fat is a mixture of sal seed fat with the fat of mowrah, phulwara and/or mango kernel. 70

4. A process according to claim 1 or 2, wherein the vegetable fat is a mixture of the fat of mowrah, phulwara and mango kernel.

5. A process according to claim 1 to 4, wherein the partial hydrogenation is carried out about 100°C–180°C. 75

6. A process according to claim 5, wherein the pressure is between atmospheric pressure and 35 lb per sq. in. 80

7. A process according to any of the preceding claims, wherein the metal catalyst is a supported fresh nickel catalyst.

8. A process according to any of the preceding claims, wherein the hardened or hydrogenated fat contains less than 2% of trisaturated glycerides. 85

9. A process according to any of the preceding claims, wherein the vegetable fat is hydrogenated to an iodine number of 33 to 36. 90

10. A process according to any of the preceding claims, wherein thermal crystallisation is carried out between 33°C and 38°C.

11. A process according to claim 10, wherein thermal crystallisation is carried out between 34 and 36°C. 95

12. A process according to any of the preceding claims, wherein sufficient high melting glycerides are removed by the thermal crystallisation to give a product melting at about 37°C. 100

13. A process according to claim 12, wherein about 15% by weight of the hardened fat is removed by the thermal crystallisation.

14. A process according to any of the preceding claims, wherein the hardened fat is maintained in a molten form. 105

15. A process according to the preceding claims, wherein the vegetable fat prior to partial hydrogenation is treated with a reagent containing sodium acetate and acetic acid buffer for removal of ellagic acid and ellagitannins. 110

16. A process for production of modified vegetable fats substantially as hereinbefore described in the foregoing Example.

17. A vegetable fat containing C₁₆, C₁₈ and C₂₀ fatty acid glycerides which has been modified by catalytic partial hydrogenation followed by thermal crystallisation at 30°C–40°C, having a sharp melting point of 37°C., an iodine value of 37 to 40, a temperature rise on solidification of 4–5°C. 120

18. A fat as claimed in claim 17 when produced by the process of any of claims 1 to 16.

19. A mixture of cocoa butter and a fat as claimed in claim 17 or 18, the proportion of the latter being 5 to 25% by weight of the mixture. 125

20. Chocolates made with a fat as claimed in claim 17 or 18 or a fat mixture as claimed in claim 19. 130

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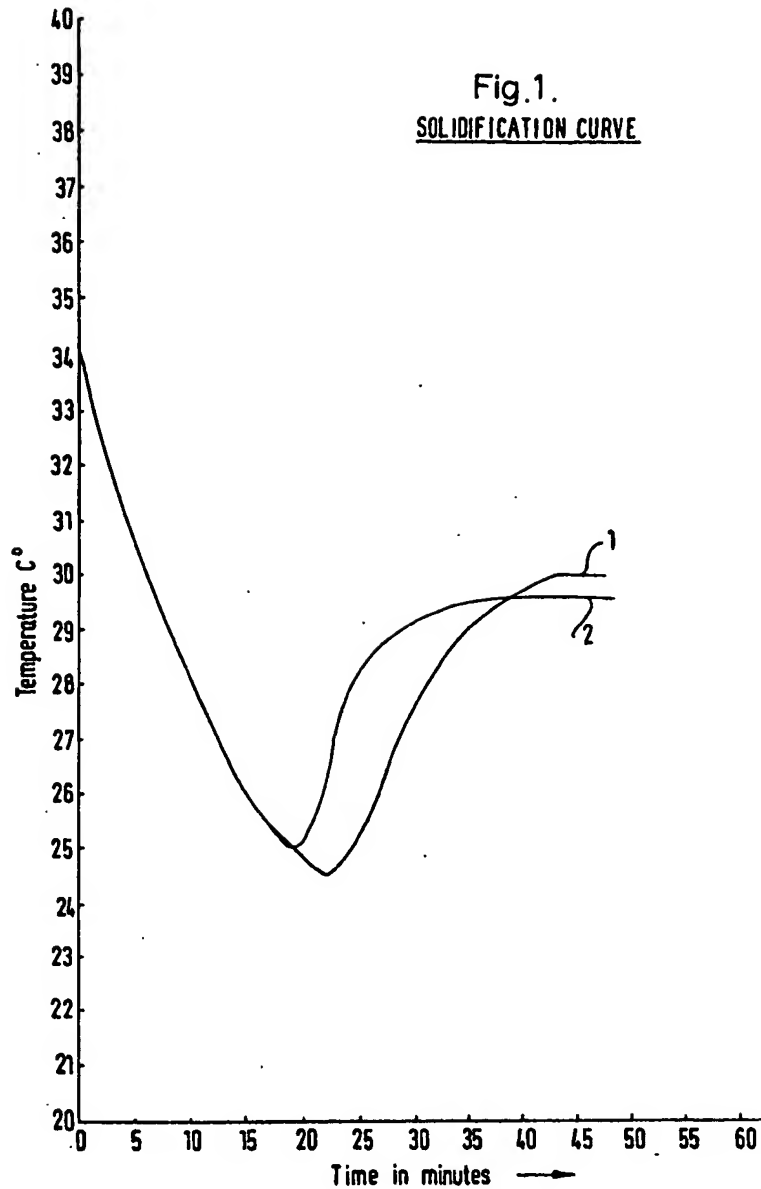
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COMPLETE SPECIFICATION

4 SHEETS

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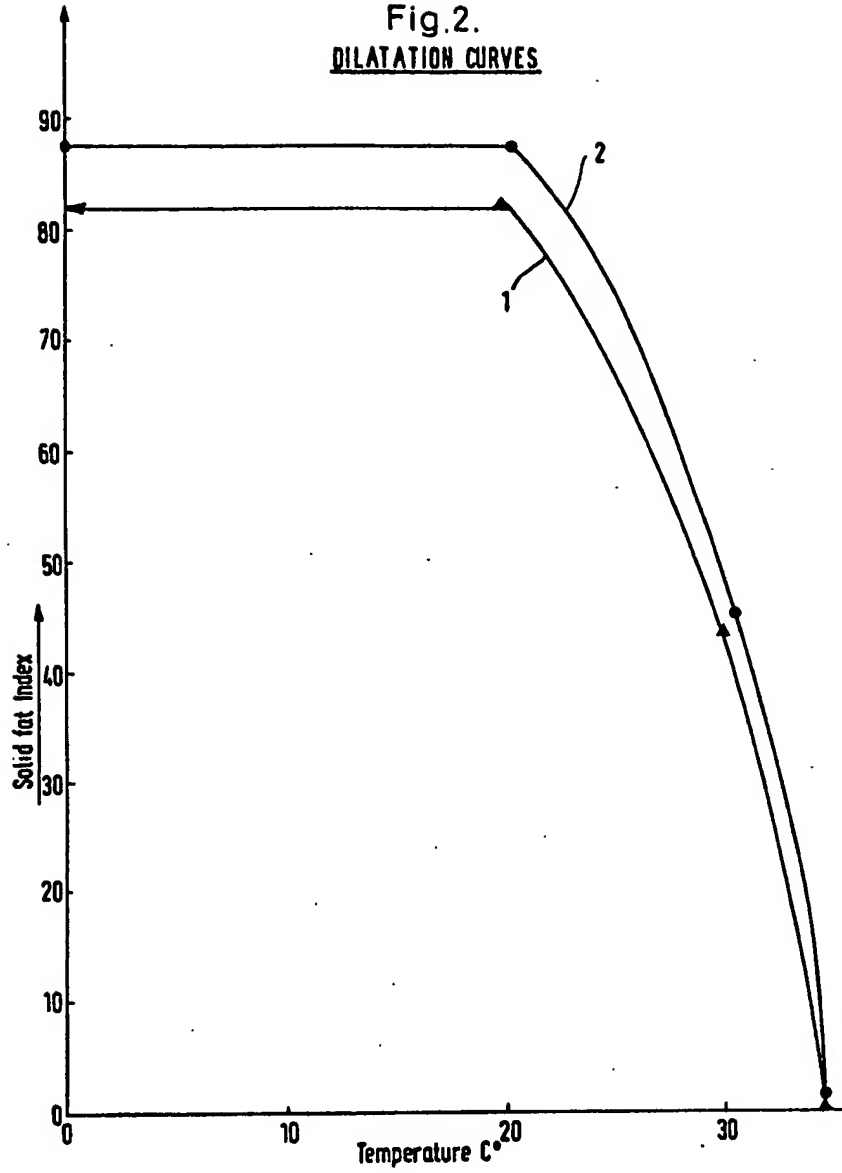
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Fig.2.
DILATATION CURVES



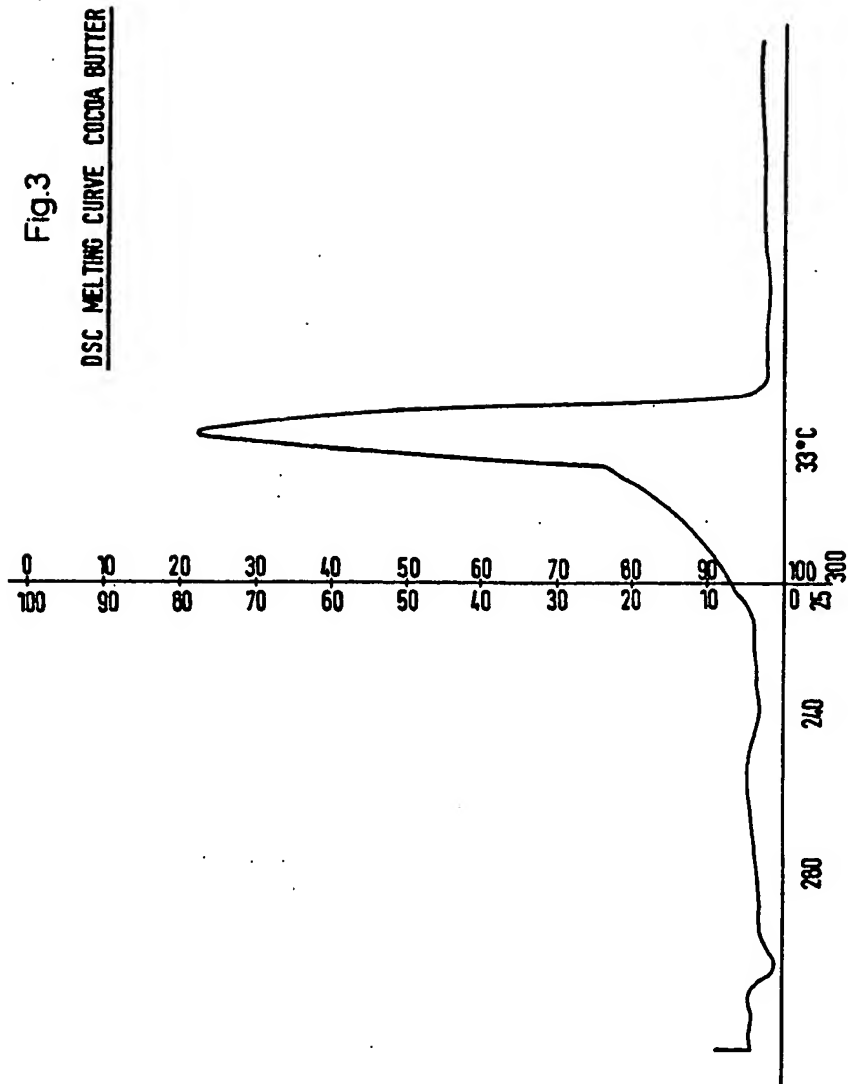
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